

Final Exam  
March 17, 2008

Law I  $\Delta U = q + w$ 

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Law II:  $dS = \frac{q_{rev}}{T}$ 

$$S = S(T, V)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Comb I, II:  $dU = TdS - PdV$ 

$$H = U + PV; \quad A = U - TS$$

$$G = H - TS; \quad dG = -SdT + VdP$$

Thermodynamic Equation of State

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}; \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P;$$

$$\mu_A = \mu_A^\circ + RT \ln \frac{P_A}{P^\circ}$$

Dalton's Law

$$P_A = \chi_A P_{Tot}; \quad P_T = \sum_A P_A; \quad G = \sum n_i \mu_i$$

$$\Delta G_{mix} = RT \sum n_i \ln \left(\frac{P_i}{P^\circ}\right)$$

$$P_A = x_A P_A^* = y_A P_{Tot} \quad \text{Raoult/Dalton Law}$$

$$n_\ell (Z - \chi) = n_v (y - Z) \quad \text{Lever Rule}$$

Calculus Identities:

$$\Delta Z = \int_{x_i}^{x_f} \left(\frac{\partial Z}{\partial x}\right)_y dx$$

$$\text{Cyclic rule: } \left(\frac{dx}{dy}\right)_z \left(\frac{dz}{dx}\right)_y \left(\frac{dy}{dz}\right)_x = -1$$

$$\frac{d(yz)}{dx} = z \frac{d(y)}{dx} + y \frac{d(z)}{dx}$$

$$\frac{dx}{dz} = \frac{dy}{dz} \frac{dx}{dy}; \quad \left(\frac{\partial x}{\partial z}\right)_a = \left(\frac{\partial y}{\partial z}\right)_a \left(\frac{\partial x}{\partial y}\right)_a$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\text{vdW Gas EoS: } P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\Delta H_{rxn}^\circ = \sum_i \nu_i \Delta H_f^\circ(i)$$

$$\Delta S_{rxn}^\circ = \sum_i \nu_i S_f^\circ(i)$$

$$dn_i = n_i - n_i^{init} = \nu_i dX$$

$$\Delta C_{P,rxn} = \sum_i \nu_i C_{P,m}(i)$$

$$\Delta H^\circ = \Delta H_{rxn}^\circ dX$$

$$\Delta G_{rxn} = \Delta G_{rxn}^\circ + RT \ln Q_P = RT \ln \frac{Q_P}{K_P}$$

$$\Delta E = \Delta E^\circ - \frac{RT}{\nu_e F} \ln Q_P \quad \text{Nernst Eqn.}$$

$$Q_P = \prod_{i=1}^N \left(\frac{P_i}{P^\circ}\right)^{\nu_i} \quad @ \text{Eq } Q_P = K_P$$

$$K_P = \left(\frac{P}{P^\circ}\right)^{\Delta \nu} \quad K_x = \left(\frac{c_o RT}{P^\circ}\right)^{\Delta \nu} K_c$$

$$\ln \left(\frac{K_P(T_2)}{K_P(T_1)}\right) = -\frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{Van't Hoff Eqn :}$$

$$\ln \left(\frac{P_2}{P_1}\right) = -\frac{\Delta H^{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{Clausius-Clapeyron}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\Delta \mu} = \frac{\Delta S}{\Delta V} \quad \text{Clapeyron}$$

Constants:

$$R = 8.3 \text{ J / mol} - \text{K}$$

$$R = 0.082 \text{ L} - \text{atm / mol} - \text{K}$$

$$R \cdot 300 = 2.5 \text{ kJ / mol}$$

$$\frac{R \cdot 300}{F} = 25 \text{ mV}$$

$$1 \text{ bar} = 10^5 \text{ Pa}$$

$$T(\text{K}) = T(\text{C}) + 273.15$$

$$F = 96,500 \text{ Coulombs/mole-e}$$

**Show your work throughout; clearly show what equations you are using, and always show units for computed quantities.**

More equations of state and Maxwell relations:

$$dU = TdS - PdV \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\frac{\Delta S_{\alpha,\beta}}{\Delta V_{\alpha,\beta}} = \frac{dP}{dT}$$

Useful equations for non-ideal gases:

$$z = \frac{PV}{RT} \quad \ln \gamma = \int_0^P \frac{\{z-1\}}{P'} dP'$$

Useful equations for ionic solutions and electrochemistry:

$$\Delta G_{rxn} = -v_e F E(V)$$

$$dq = Idt$$

$$dG = \Delta G_{rxn} dX$$

$$I = \frac{1}{2} (v_+ z_+^2 + v_- z_-^2) m$$

$$\ln \gamma_{\pm} = -1.173 |z_+ z_-| \sqrt{I}$$

$$\ln \gamma_{\pm} = 2.3 \cdot \log_{10} \gamma_{\pm}$$

$$\text{Appx Values} \quad \log_{10} 5 = .7 \quad \ln 2 = .7 \quad \log_{10} 2 = .3$$

$$E = E^o - \frac{RT}{v_e F} \ln Q = -\frac{RT}{v_e F} \ln \frac{Q}{K} \quad Q = \prod_{i=1}^N (a_i)^{v_i} = \prod_{i=1}^N \left( \gamma_i \frac{c_i}{c_o} \right)^{v_i}$$

$$\mu_A = \mu_A^o + RT \ln a_A$$

$$a_A = \gamma_A x_A$$

Cu half cell reduction potential:  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad E^o = 0.34V$

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Q1) a) For any process (no constraints) what is the thermodynamic criterion of spontaneity?

b) For any process carried out at constant pressure and temperature, what is the specific criterion of spontaneity?

c) In a chemical reaction (carried out at constant pressure and temperature) what is the criterion of equilibrium?

d) How can you use  $\Delta G$  to define chemical equilibrium?

e) How can you use  $\Delta G_{rxn}$  to define chemical equilibrium?

f) How can you use  $\Delta G_{rxn}^o$  to define chemical equilibrium?

d) Fuel cells (and the hydrogen economy) will run on the chemical reaction

$2H_2 + O_2 \rightleftharpoons 2H_2O$  for which  $\Delta G_{rxn}^o = -475 \text{ kJ/mole}$ . Analyze the following statement:

The fact that  $\Delta G_{rxn}^o$  is far from zero implies that the system is far away from equilibrium.

e) If I have a fuel cell set up so that all chemical species are at unit activity, and I run it long enough to consume 0.01 moles of Hydrogen gas, what is the maximum electrical work that can be obtained from the reaction?

Q2) Consider a gas with the van der Waals; equation of state for which the constant  $b = 0$ .

a) Express the compressibility,  $z$ , for this van der Waals gas ( $b = 0$ )

b) Develop an exact expression for the fugacity (or activity) coefficient for this case.

c) From the complete expression, (part a) explain why the fugacity (or activity) coefficient for this gas is always positive but less than 1.

d) What is the physical interpretation of a fugacity (or activity) coefficient less than one?

e) Assume that  $nRT > a/V$ , (using the result from part b) and derive an approximate expression for the fugacity coefficient.

Q3) The vapor pressure of a liquid can be written in an empirical form known as the Antoine equation, where the parameters  $A_1$ ,  $A_2$ , and  $A_3$  are constants determined from measurements:

$$\ln\left(\frac{P}{P_o}\right) = A_1 - \frac{A_2}{T - A_3}$$

[Hint: Use the Clausius-Clapeyron Equation as a guide. Consider  $T$ ,  $A_2$ , and  $A_3$  to be in units of Kelvin ]

Starting with this equation derive an equation (in terms of the constants of the Antoine equation) giving  $\Delta H_{\text{vaporization}}$  as a function of temperature.

Q4) Benzene and Toluene form an ideal solution at 300K (i.e. the mixture obeys Raoult's law).  $P_{toluene}^* = 30.0Torr$  and  $P_{Benzene}^* = 90.0Torr$ . The liquid is composed of 2 moles of toluene and 3 moles of benzene. [You may want to sketch a pressure v. composition diagram.]

a) At what pressure does the first vapor form?

b) What is the composition of the first trace of vapor formed?

c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?

d) What is the composition of the last trace of liquid?

Q5) a) Solid silver sulfate can dissolve only sparingly in water as  $Ag_2SO_4(s) \rightleftharpoons 2Ag^{+1} + SO_4^{2-}$  because:  $K_{sp}(Ag_2SO_4) = 4 \cdot 10^{-6}$ . Compute the molar (or molal) solubility of this salt assuming that it behaves as an ideal salt.

b) Compute the ionic strength of this saturated solution of silver sulfate.

c) Estimate the activity coefficient for this solution using the Debye-Hückel limiting law.

d) Does the solubility increase or decrease when the activity coefficient is included in the calculation. Explain your reasoning with the appropriate equations.

Q6) A van der Waals gas is allowed to expand adiabatically and reversibly so that the pressure decreases from its initial pressure and the volume increases.

a) What state functions do not change in this process, for any ideal or real gas?

b) Assuming that the entropy is invariant over the process then it follows that  $\int_A^B dS = 0$ .

Use this constraint and the total derivative of the entropy in terms of T and V, to develop an expression that relates the temperature change to the volume change. (Leave the result in the integral form. Use the appropriate Maxwell relation to develop an expression that uses only heat capacity, P, V, and T).

c) Assume that the heat capacity  $\left( C_V = \frac{4}{2} nR \right)$  is independent of temperature and find a relation between the temperature change and the volume change for this process.

d) If the volume expands from  $V_{I,m} = 6b$  to  $V_{F,m} = 11b$  (here  $b$  is the van der Waals parameter) and  $\frac{a}{V_{I,m}} = 0.1 \text{ Joules/mol}$ , for the vdW gas what is the temperature change as a ratio of the final to the initial temperature?

Q7) Consider a battery described by:  $Cu | Cu^{+2} || Cu^{+2} | Cu$  Assume that the battery is composed of two solutions (in separate containers) of equal volume, one liter, with Cu plates in them. One solution is 0.1 M in  $CuSO_4$  and the other is 0.01M in  $CuSO_4$ . (Additionally there is a salt bridge between the two solutions and a wire with a volt meter connecting the two Cu plates.)

a) What is the standard EMF,  $E^\circ$ , of such a battery:

b) Explain why there is any voltage to this batter at all.

c) Will oxidation or reduction occur in the solution with the 0.01M concentration? Explain.

d) What is the voltage of this battery at  $T = 300K$  ?

e) By what fraction would the voltage change if the temperature were increased by 10%.

f) Determine the reaction entropy  $\Delta S_{rxn}$  for this system:

- g) Determine the reaction enthalpy  $\Delta H_{rxn}$  for this system:
- h) When the battery is exhausted, what will the concentration of  $CuSO_4$  be in the two solutions?
- i) What is the maximum amount of electrical work you can get from the battery assuming that it will perform at peak value for the entire running of the battery?
- j) In some possible electrochemical cells, unlike the Cu-Cu battery, the change in cell potential with temperature is very small. What does this tell you about the thermodynamics of the cell reaction for these batteries?
- k) Would such a battery have diminished power output at low temperatures? Why or why not?

## Q8) Differentials

a) Starting with the van der Waals equation of state, find an expression for the total differential  $dP$  in terms of  $dT$  and  $dV$ .

b) By calculating the mixed partial derivatives  $\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial V}\right)_T\right)_V$  and  $\left(\frac{\partial}{\partial V}\left(\frac{\partial P}{\partial T}\right)_V\right)_T$ , determine if  $dP$  is an exact differential.

c) Find  $\left(\frac{\partial T}{\partial P}\right)_V$  for the van der Waals (vdW) gas. Express your answer in terms of the variables  $P, V$  and  $T$ , and the other constants of the vdW Gas. Do not express your answer in terms of  $\beta$  and  $\kappa$ . [Hint As a check: of  $P, V$  and  $T$ , the result should only depend on  $V$ .]